Redox Reactions and Electrochemistry

10.1 Galavanic or Voltaic Cells

a) Anode/Cathode/Salt Bridge

b) Cell Notations

c) Determining Cell Potential/Cell Voltage/Electromotive force (emf)

10.2 Application :types of batteries

Application (10.2) : Corrosion

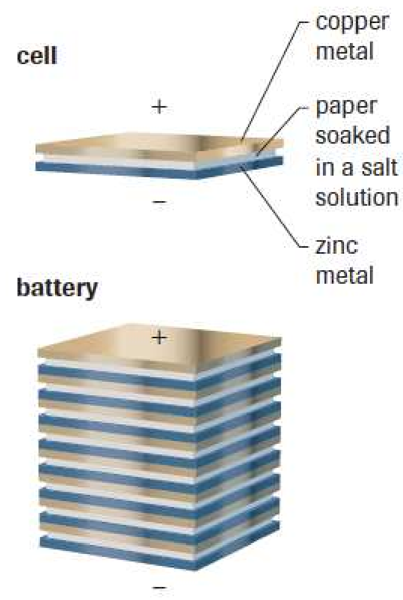
Batteries

Fuel Cells

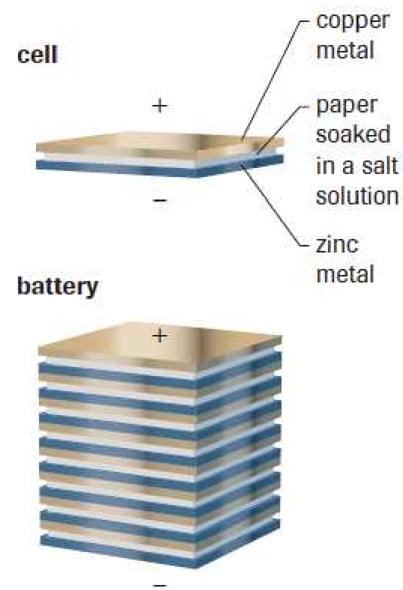
Application (10.3) Electrolytic Cells

Application to Electrochemistry

- An *electric cell* converts chemical energy into electrical energy
  - **Alessandro Volta** invented the first electric cell but got his inspiration from **Luigi Galvani**. Galvani's crucial observation was that two different metals could make the muscles of a frog's legs twitch. Unfortunately, Galvani thought this was due to some mysterious "animal electricity". It was Volta who recognized this experiment's potential.
  - An electric cell produces very little electricity, so Volta came u design:
- A *battery* is defined as two or more electric cells (series to produce a steady flow of current
  - V f brine (Na(owl to anot
  - F wo metals s

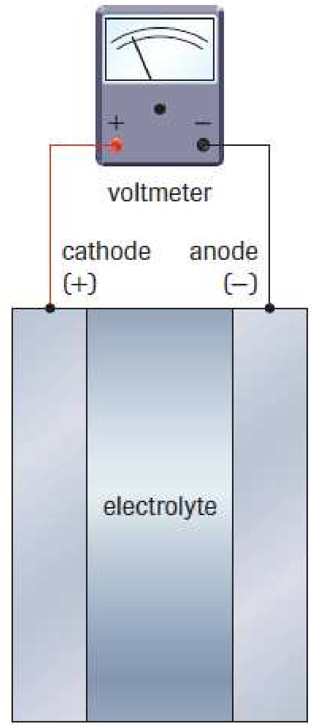


- Alessandro Volta’s invention was an immediate technological success because it produced electric current more simply and reliably than methods that depended on static electricity.
- It also produced a steady electric current –something no other device could do.



- Electric cells are composed of two **electrodes** – solid electrical conductors and at least one **electrolyte** (aqueous electrical conductor)

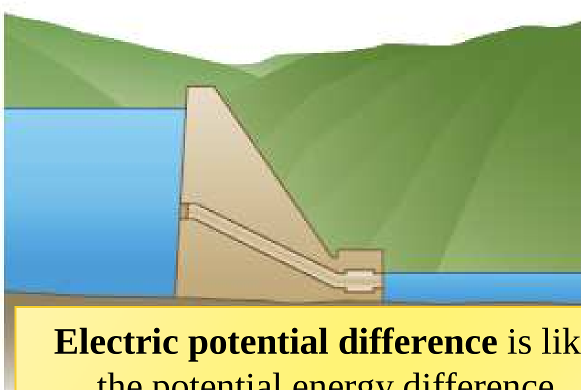
- In current cells, the electrolyte is often a moist paste *(just enough water is added so that the ions can move)*. Sometimes one electrode is the cell container.



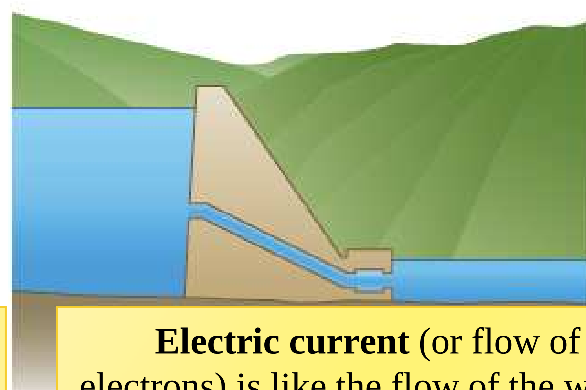
- The positive electrode is defined as the **cathode** and the negative electrode is defined as the **anode**
  - The electrons flow through the external circuit from the anode to the cathode.To test the voltage of a battery, the red(+) lead is connected to the cathode (+ electrode), and the black(-) lead is connected to the anode (- electrode)

- A <u>voltmeter</u> is a device that measures the energy difference, per unit charge, between any two points in an electric circuit (called **electric potential difference)**
  - I.e. A 9V battery releases 6X as much energy compared with the electrons from a 1.5V battery.
  - The voltage of a cell depends mainly on the chemical composition of the reactants in the cell

- An <u>ammeter</u> is a device that measures the rate of flow of charge past a point in an electrical circuit (called **electric current**)
  - The larger the electric cell, the greater current that can be produced



Electric potential difference is like the potential energy difference between 1kg of water at the top of the dam and 1kg of water at the bottom of the dam.



Electric current (or flow of electrons) is like the flow of the water. A larger drain would be like a larger electric cell, allowing more water (or electrons) to flow.

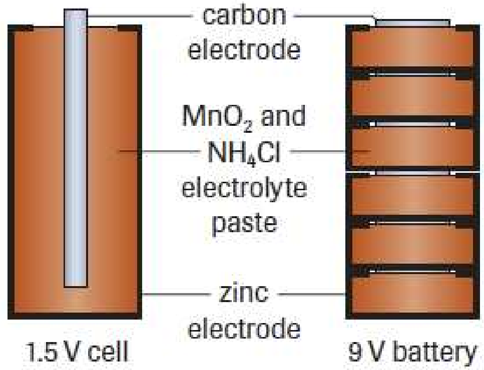


Figure 6
Like a flashlight D cell, the zinc chloride dry cell on the left has a voltage of 1.5 V. The 9 V battery on the right is made up of six 1.5 V dry cells in series.

Primary cells cannot be recharged, but are relatively inexpensive

Secondary cells can be recharged using electricity, but are expensive

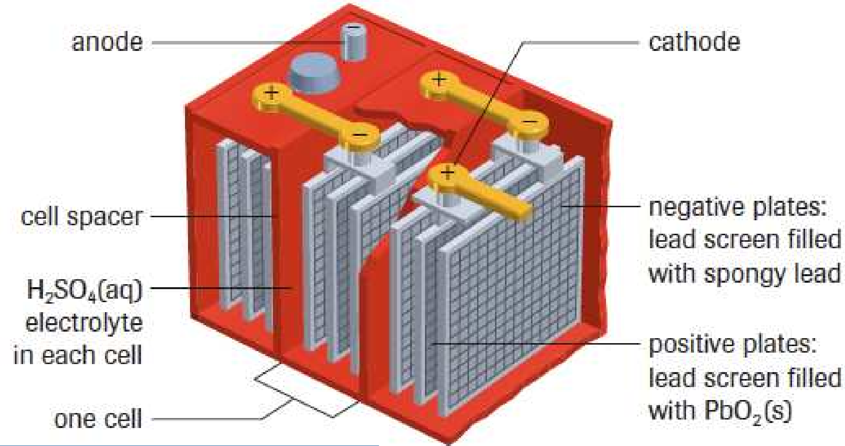


Figure 7
The anodes of a lead-acid car battery are composed of spongy lead and the cathodes are composed of lead(IV) oxide on a metal screen. The large electrode surface area is designed to deliver sufficient current to start a car engine.

Learning Tip

Discharging a cell or battery is like letting the water spontaneously run out from the higher level behind a dam. Charging (or recharging) is like pumping the water up behind the dam. This is not a spontaneous process and requires energy.

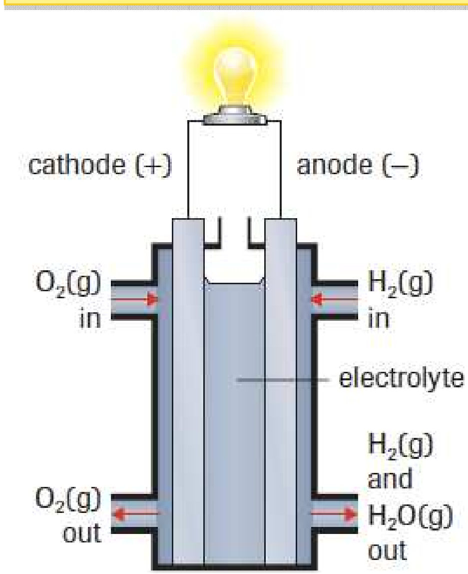


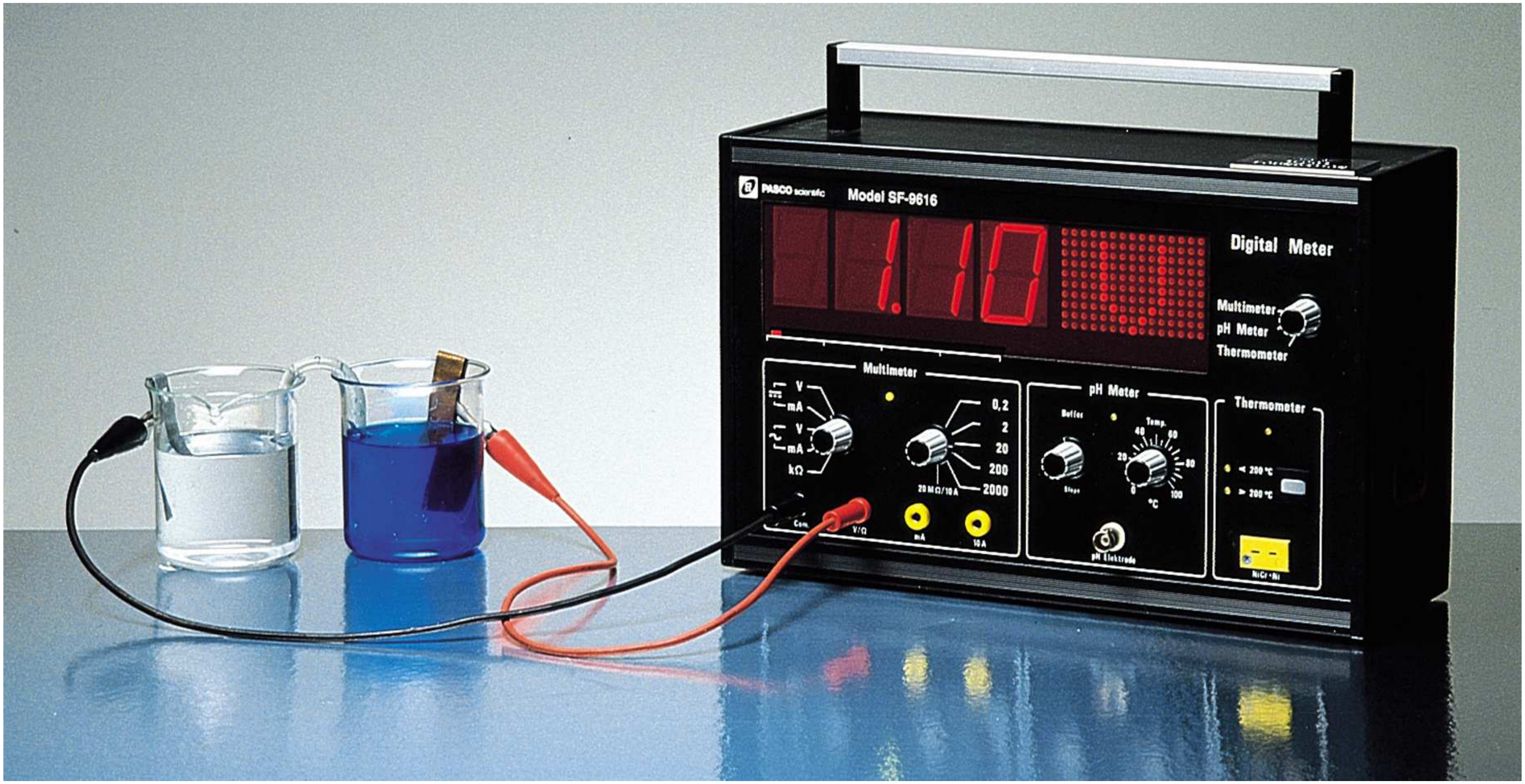
Figure 8
Hydrogen and oxygen gases are continuously pumped into this hydrogen-oxygen fuel cell. Each g reacts at a different electrode. Unused gases are recycled.

Table 3 Efficiencies of Different Technologies*

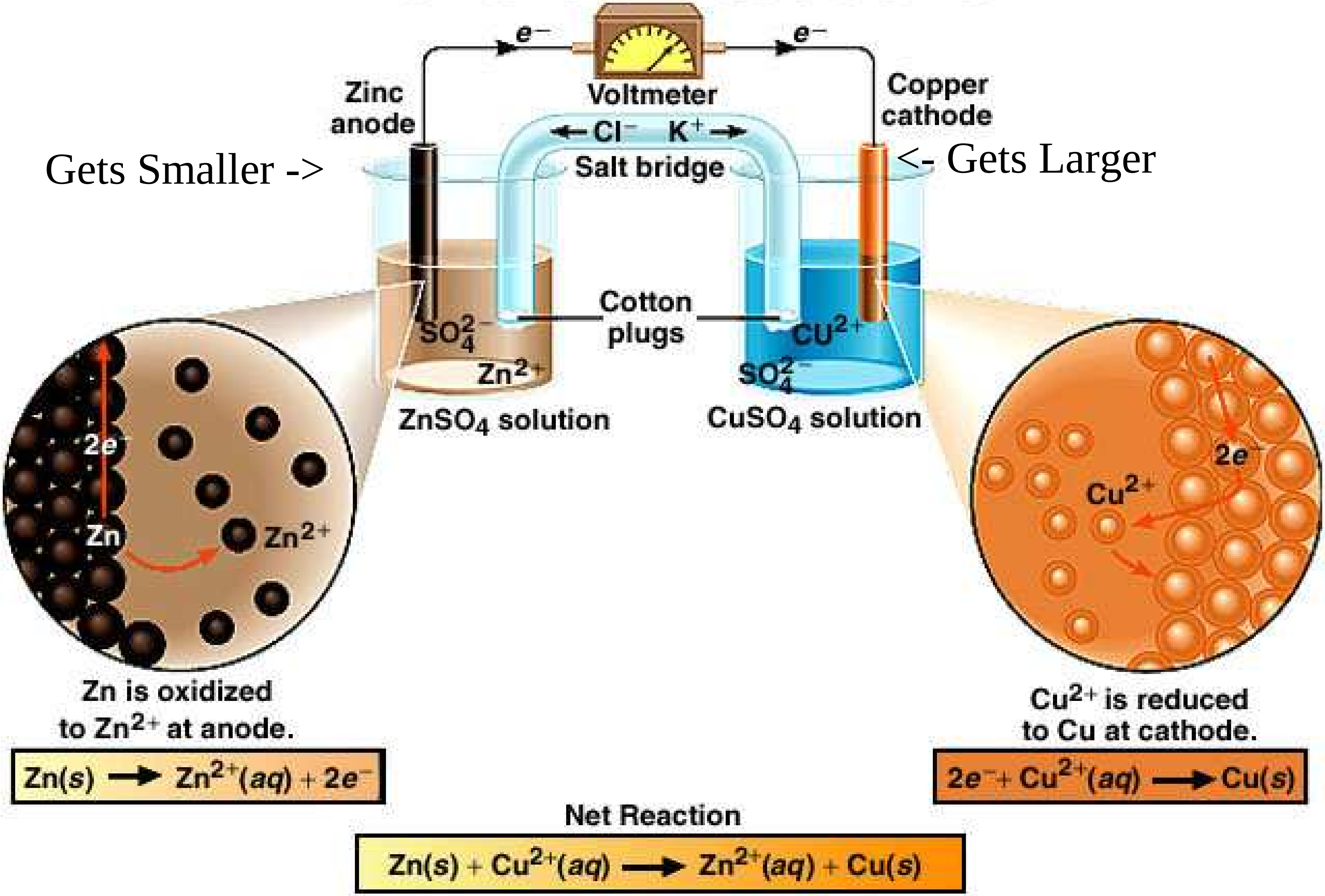
Technology	Efficiency*
fuel cells	40–70%
electric power plants	30–40%
automobile engines	17–23%
gasoline lawn mower	about 12%

*Efficiency is the fraction of the maximum available energy that is actually usable.

Fuel cells produce electricity by the reaction of a fuel that is continuously supplied.
More efficient, and used for NASA vehicles, but still too expensive for general or commercial applications


Model SF-9616
1.10
Digital Meter
Multimeter
pH Meter
Thermometer
Multimeter
pH Meter
Thermometer

Zn and Cu Reactions



Voltaic Cell Animation

Anode; Site of Oxidation
Cathode; Site of Reduction

AnOx or both vowels
Red Cat or both consonants

Direction of electron flow; anode to cathode (alphabetical)

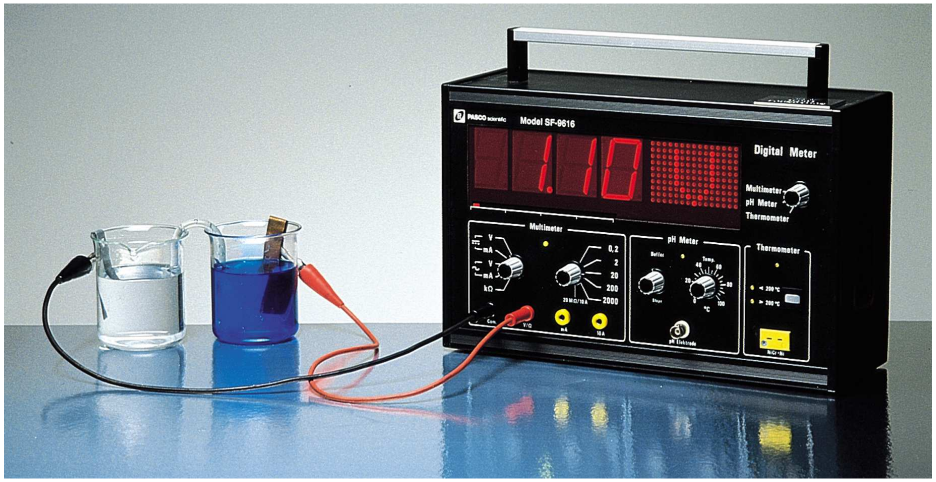
Salt Bridge; Maintains electrical neutrality
+ ion migrates to cathode
- ion migrates to anode

Cell Notation

1. Anode
2. Salt Bridge
3. Cathode

Anode | Salt Bridge | Cathode

| : symbol is used whenever there is a different phase



Cell Notation

$$Zn\ (s) + Cu^{2+}\ (aq) \longrightarrow Cu\ (s) + Zn^{2+}\ (aq)$$

$$[Cu^{2+}] = 1\ M\ \&\ [Zn^{2+}] = 1\ M$$

$$Zn\ (s)\ |\ Zn^{2+}\ (1\ M)\ ||\ Cu^{2+}\ (1\ M)\ |\ Cu\ (s)$$

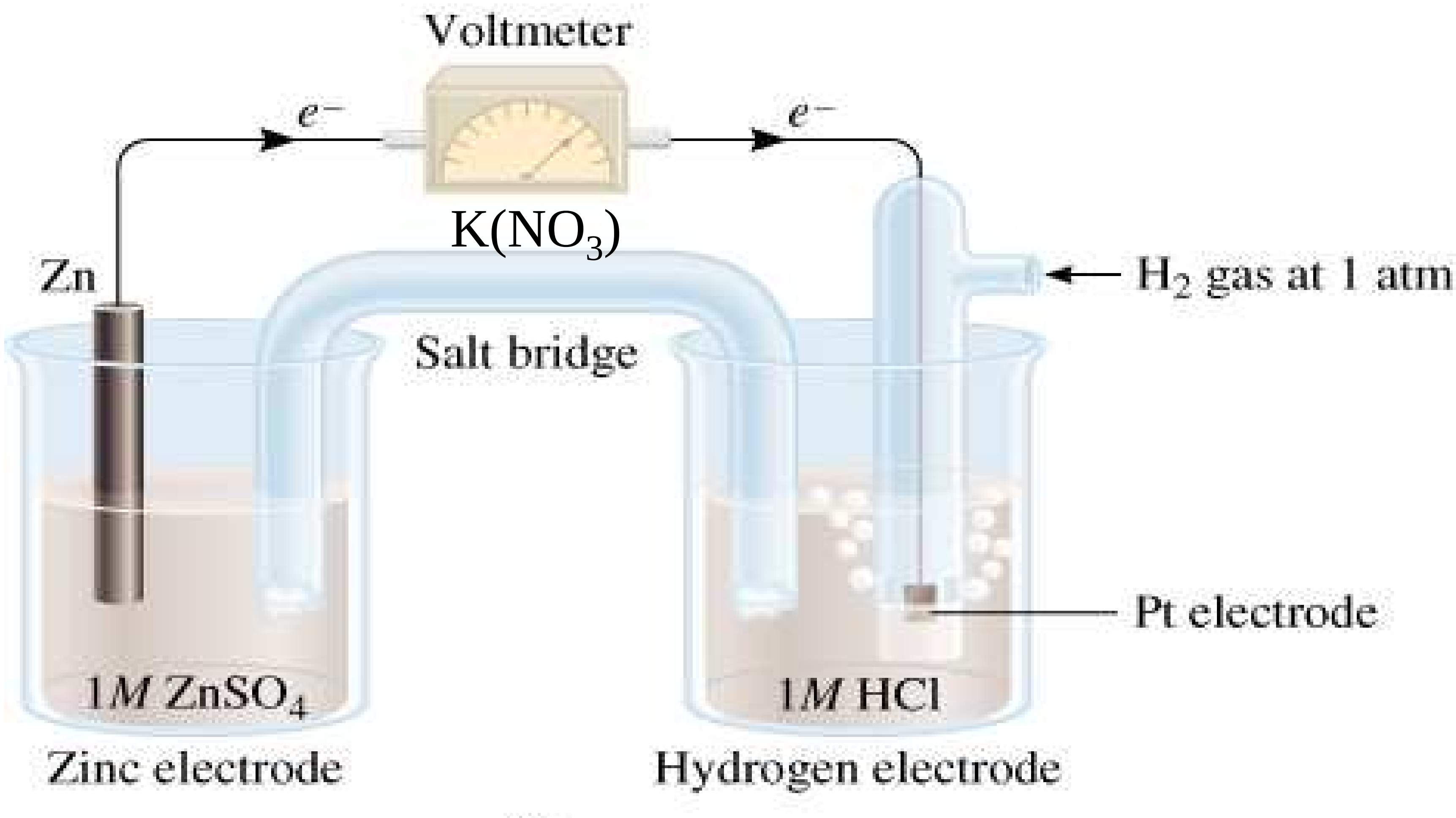
anode cathode

More detail..

$$Zn\ (s)|\ Zn^{+2}\ (aq,\ 1M)|\ K(NO_3)\ (saturated)|Cu^{+2}(aq,\ 1M)|Cu(s)$$

anode Salt bridge cathode

$\underline{Zn (s) + 2 H^+(aq) \rightarrow H_2 (g) + Zn^{+2} (aq)}$

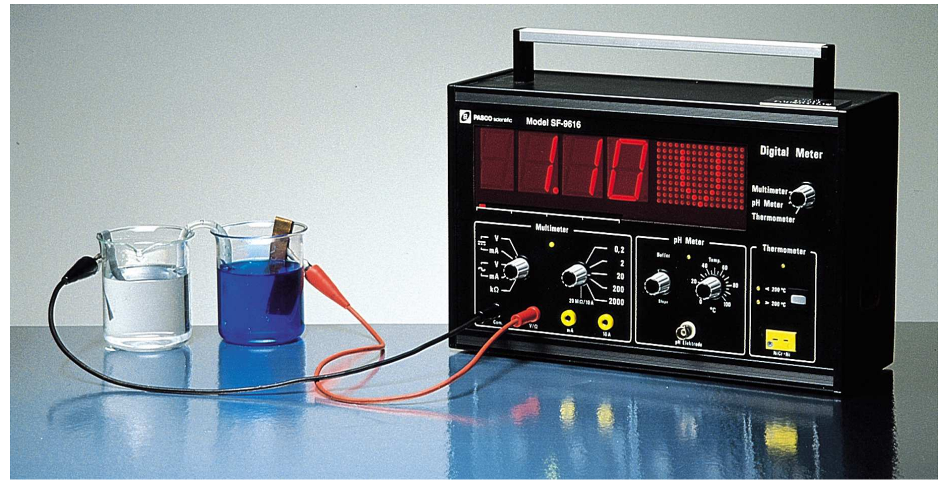


$Zn(s)| Zn^{+2}|KNO_3|H^+(aq)|H_2(g)|Pt$

Electrochemical Cells

The difference in electrical potential between the anode and cathode is called:

- ***cell voltage***
- ***electromotive force (emf)***
- ***cell potential***



$$E^0_{Cell} = E^0_{oxidation} + E^0_{reduction}$$

UNITS: Volts

$$\text{Volt (V)} = \frac{\text{Joule (J)}}{\text{Coulomb, C}}$$

e 19.1 Standard Reduction Potentials at 25°C*

Half-Reaction	$E°$(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07

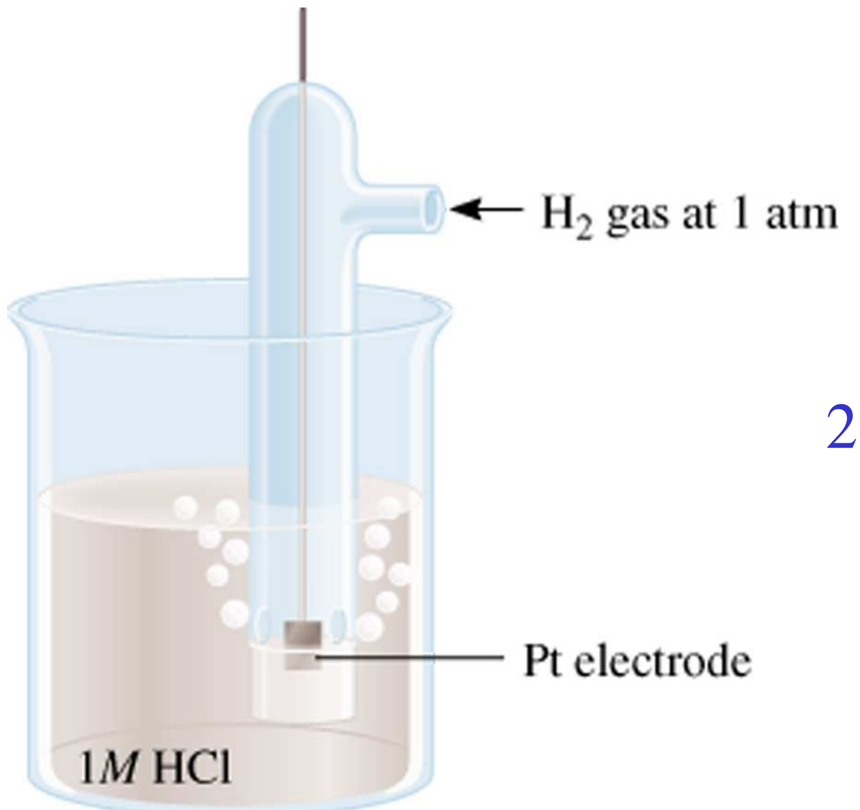
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20

$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83

$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Standard Electrode Potentials

Standard reduction potential (E^0) is the voltage associated with a **reduction reaction** at an electrode when all solutes are 1 *M* and all gases are at 1 atm.

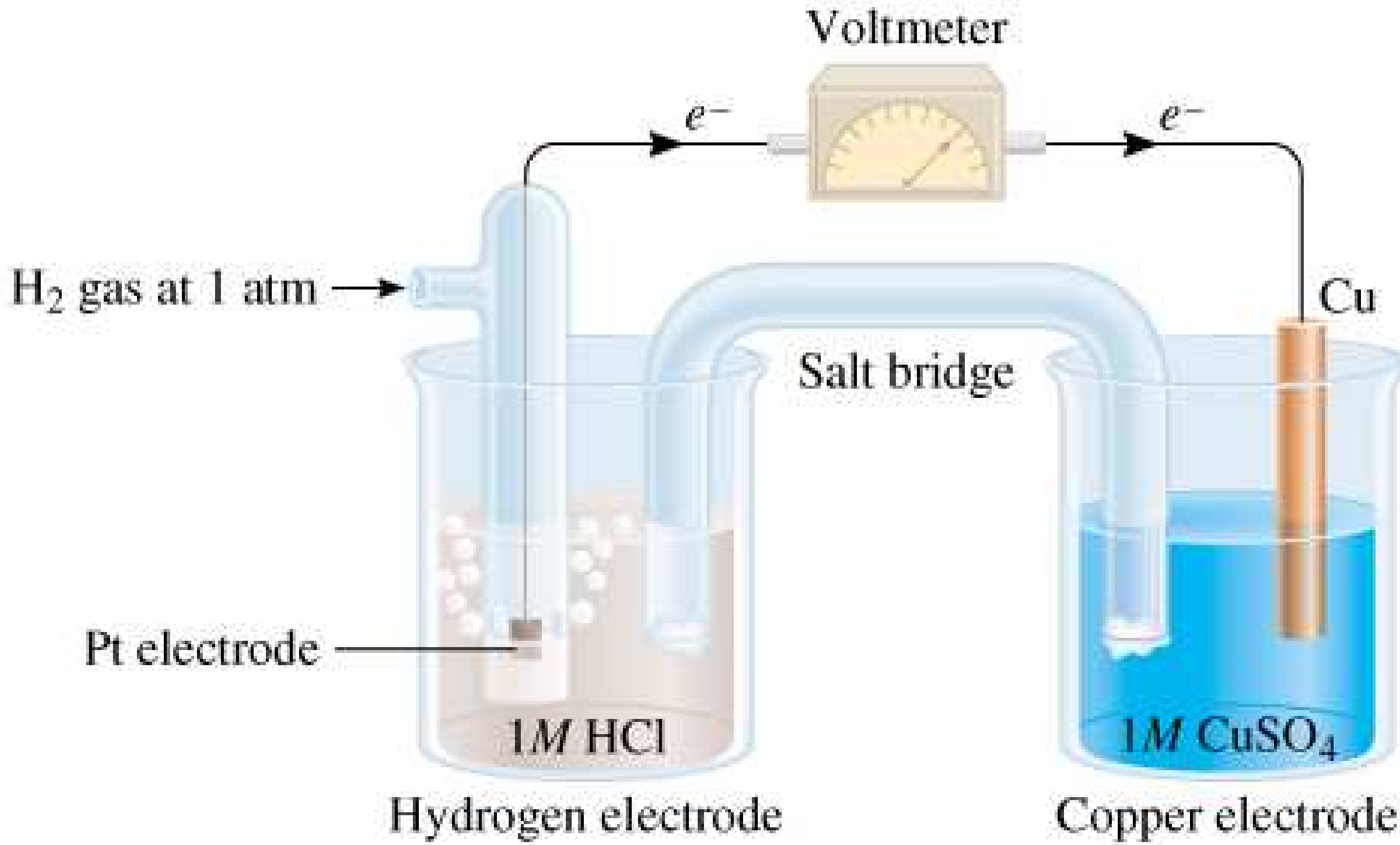


Standard hydrogen electrode (SHE)

Reduction Reaction

$$2e^- + 2H^+ (1\ M) \longrightarrow H_2\ (1\ atm)$$

$$E^0 = 0\ V$$


Voltmeter
e^-
e^-
H_2 gas at 1 atm
Cu
Salt bridge
Pt electrode
1*M* HCl
1*M* $CuSO_4$
Hydrogen electrode
Copper electrode

Determining if Redox Reaction is Spontaneous

- + $E°_{CELL}$; spontaneous reaction
- - $E°_{CELL}$; nonspontaneous reaction

More positive $E°_{CELL}$; stronger oxidizing agent or more likely to be reduced

Table 19.1 **Standard Reduction Potentials at 25°C***

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$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
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$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
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$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Increasing strength as oxidizing agent (↑)

Increasing strength as reducing agent (↓)

* For all half-reactions the concentration is 1 M for dissolved species and the pressure is 1 atm for gases. These are the standard-state values.

- E^0 is for the reaction as written
- The half-cell reactions are reversible
- The sign of E^0 changes when the reaction is reversed
- Changing the stoichiometric coefficients of a half-cell reaction ***does not*** change the value of E^0
- The more positive E^0 the greater the tendency for the substance to be reduced

Standard Potentials (cont.)

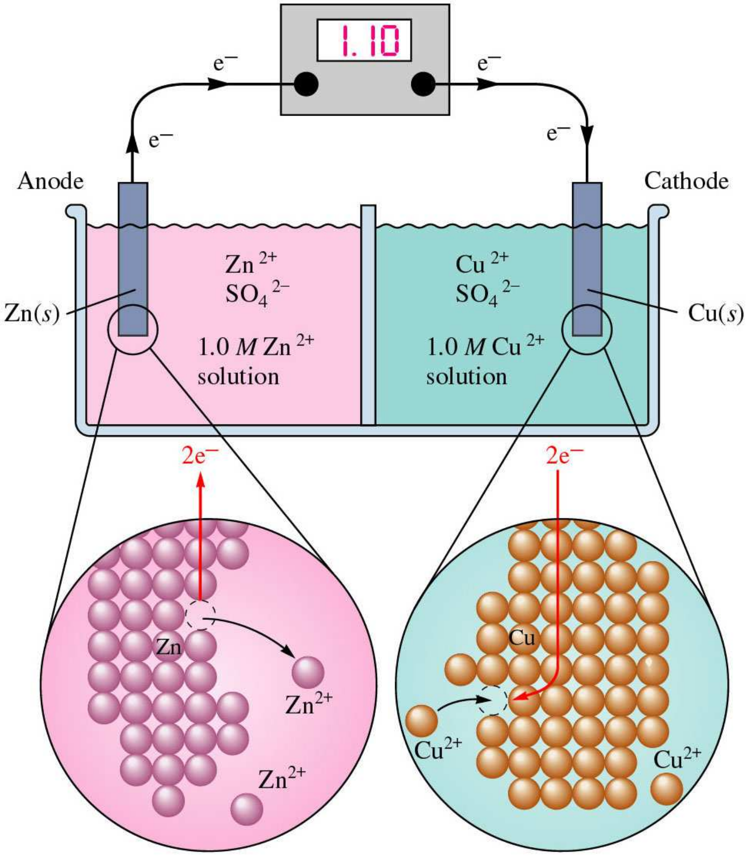
- If in constructing an electrochemical cell, you need to write the reaction as a oxidation instead of a reduction, the sign of the 1/2 cell potential changes.

$$Zn^{+2} + 2e^{-} \longrightarrow Zn \qquad E° = -0.76\ V$$

$$Zn \longrightarrow Zn^{+2} + 2e- \qquad E° = +0.76\ V$$

- 1/2 cell potentials are intensive variables. As such, you do NOT multiply them by any coefficients when balancing reactions.

Writing Galvanic Cells (cont.)



Shorthand Notation

$$Zn|Zn^{+2}||Cu^{+2}|Cu$$

Anode

Cathode

Salt bridge

Predicting Galvanic Cells

- Given two 1/2 cell reactions, how can one construct a galvanic cell?

- Need to compare the reduction potentials of the two half cells.

- Turn the reaction for the weaker reduction (smaller $E°_{1/2}$) and turn it into an oxidation. This reaction will be the anode, the other the cathode.

Predicting Galvanic Cells (cont.)

- Example. Describe a galvanic cell based on the following:

$$Ag^{+} + e^{-} \longrightarrow Ag \qquad E°_{1/2} = 0.80\ V$$

$$Fe^{+3} + e^{-} \longrightarrow Fe^{+2} \qquad E°_{1/2} = 0.77\ V$$

Weaker reducing agent – turn it around

$$Ag^{+} + Fe^{+2} \longrightarrow Ag + Fe^{+3} \qquad E°_{cell} = 0.03\ V$$

$E°_{cell} > 0$….cell is galvanic

Another Example

- For the following reaction, identify the two half cells, and use these half cells to construct a galvanic cell

$$3Fe^{+2}(aq) \longrightarrow Fe(s) + 2Fe^{+3}(aq)$$

+2 0 +3 oxidation

reduction

$$Fe^{+2}(aq) + 2e^- \longrightarrow Fe(s) \qquad E° = -0.44\ V$$

$$Fe^{+3}(aq) + e^- \longrightarrow Fe^{+2}(aq) \qquad E° = +0.77\ V$$

Another Example (cont.)

weaker reduction – turn it around

$$Fe^{+2}(aq) + 2e^- \longrightarrow Fe(s) \qquad E° = -0.44\ V$$

2 x $$Fe^{+3}(aq) + e^- \longrightarrow Fe^{+2}(aq) \qquad E° = +0.77\ V$$

$$2Fe^{+3}(aq) + Fe(s) \longrightarrow 3Fe^{+2}(aq) \qquad E°_{cell} = 1.21\ V$$

$$Fe(s) \longrightarrow Fe^{+2}(aq) + 2e^- \qquad E° = +0.44\ V$$

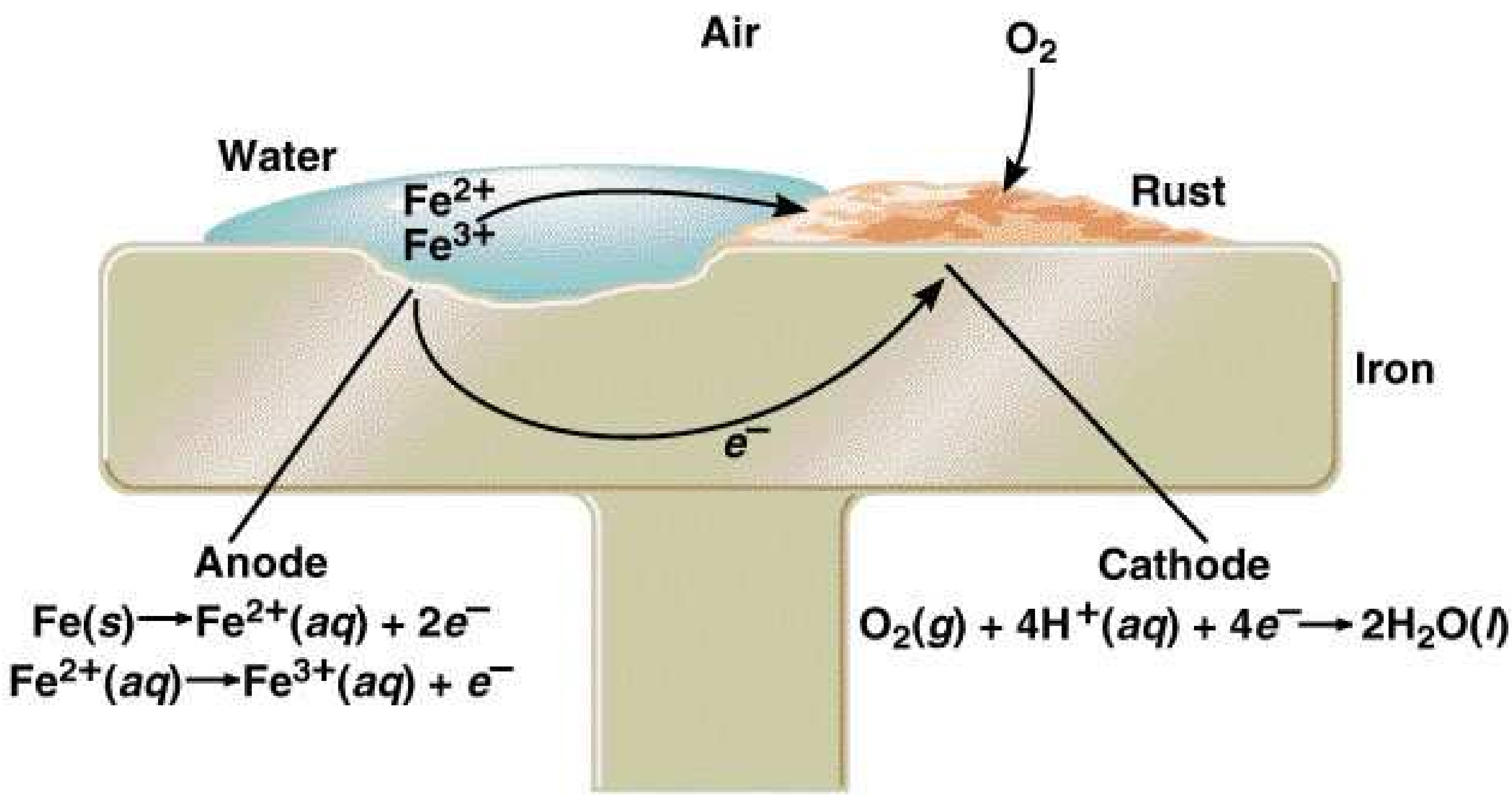
Corrosion – Deterioration of Metals by Electrochemical Process

Rusted Ship

Corrosion – Deterioration of Metals by Electrochemical Process

Half-tarnished Silver Dish

Rust Formation



Cathodic Protection

Iron Nail with Zinc

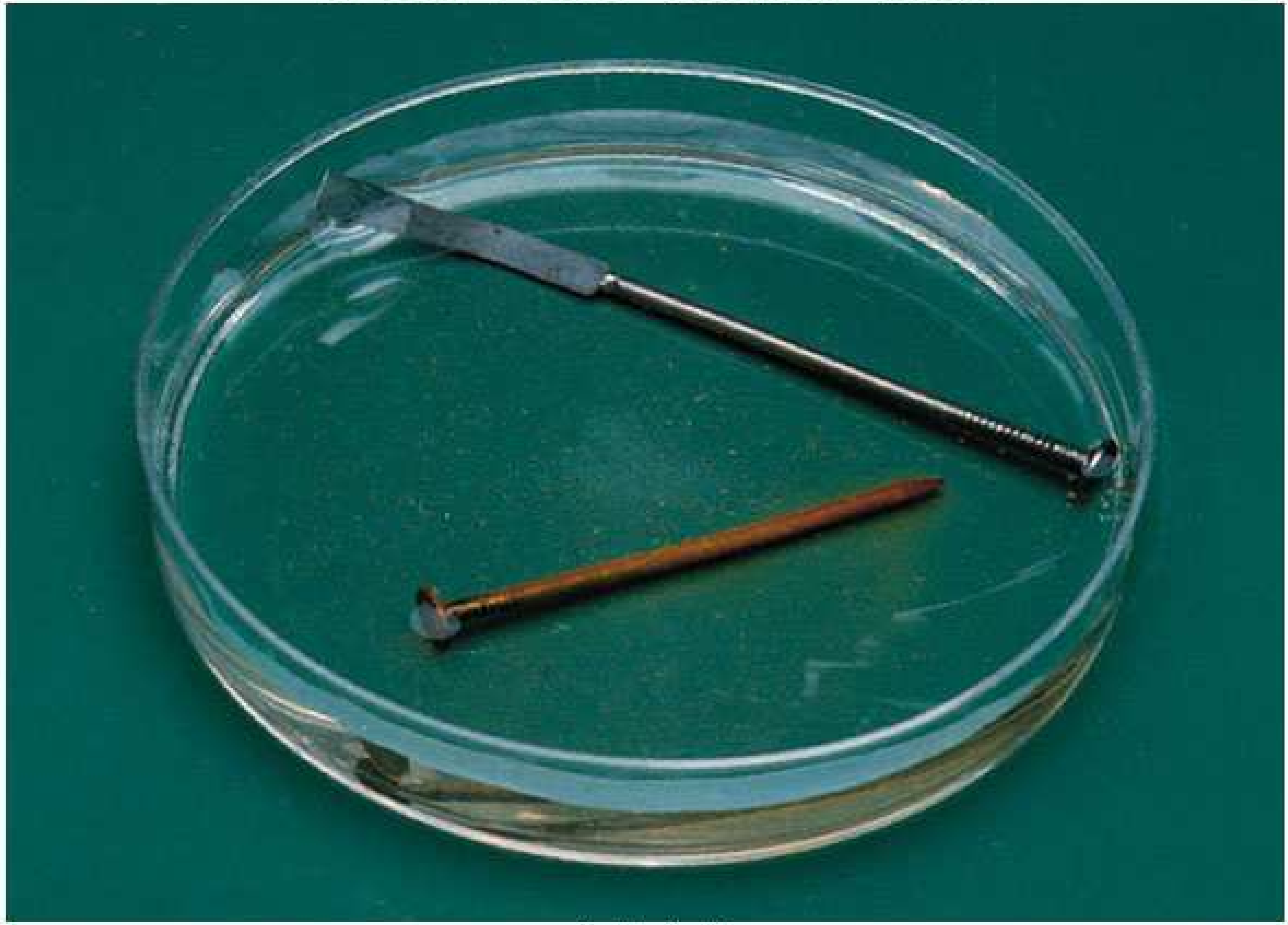


Photo by Ken Karp

Abbreviated Standard Reduction Potential Table

$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
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$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

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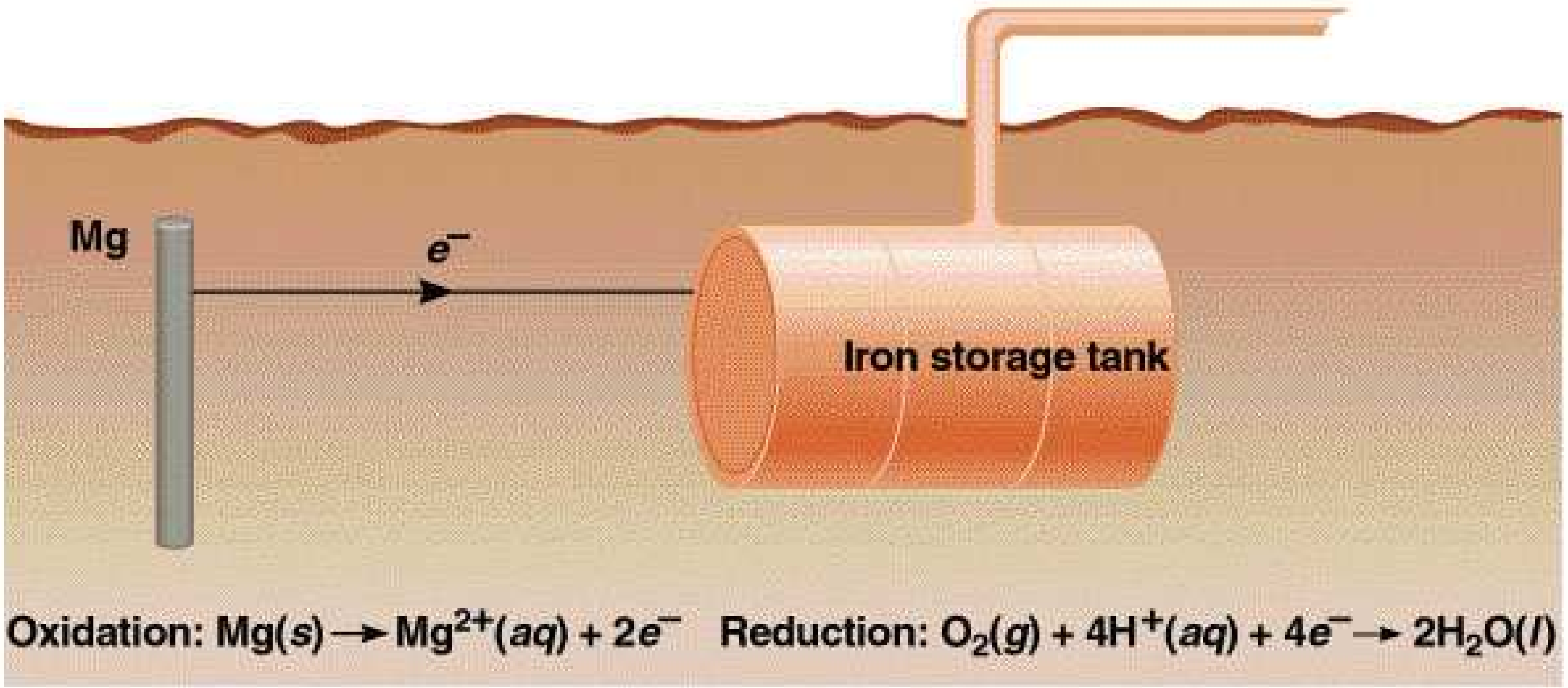
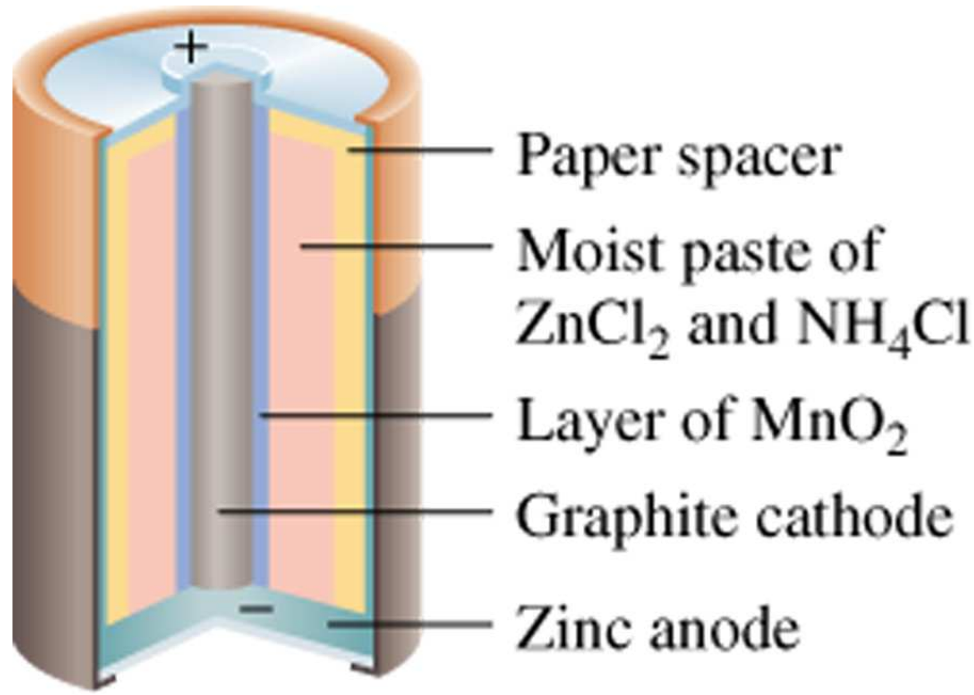
Cathodic Protection of an Iron Storage Tank



Batteries

Dry cell

Leclanché cell



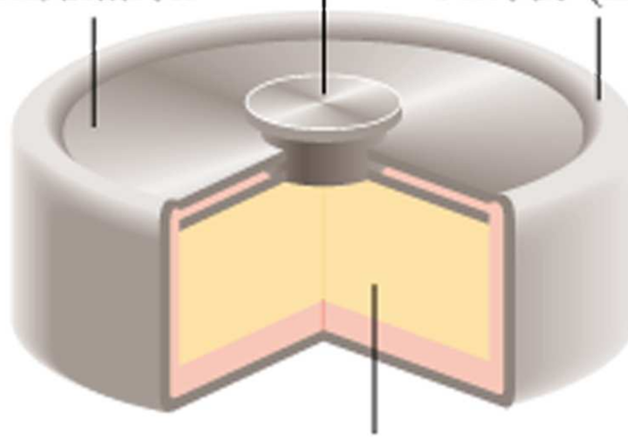
Anode: $Zn\ (s) \longrightarrow Zn^{2+}\ (aq) + 2e^-$

Cathode: $2NH_4^+\ (aq) + 2MnO_2\ (s) + 2e^- \longrightarrow Mn_2O_3\ (s) + 2NH_3\ (aq) + H_2O\ (l)$

$$Zn\ (s) + 2NH_4\ (aq) + 2MnO_2\ (s) \longrightarrow Zn^{2+}\ (aq) + 2NH_3\ (aq) + H_2O\ (l) + Mn_2O_3\ (s)$$

Batteries

Mercury Battery



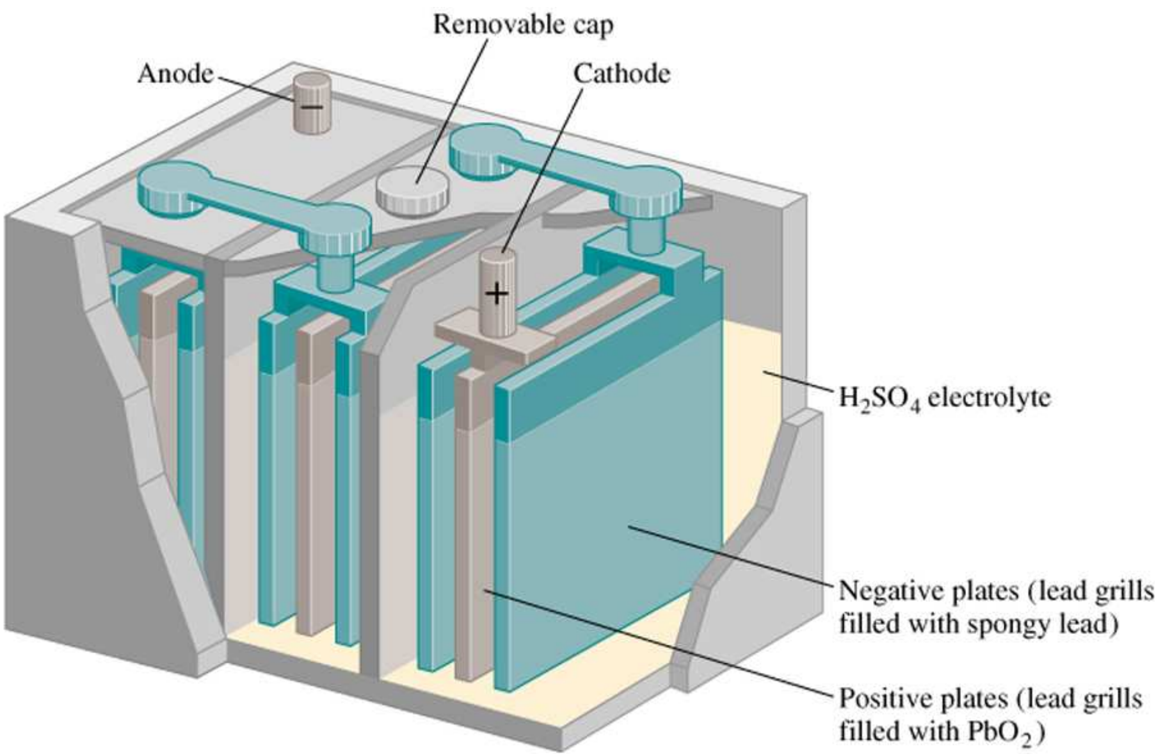
Anode: $Zn(Hg) + 2OH^- (aq) \longrightarrow ZnO (s) + H_2O (l) + 2e^-$

Cathode: $HgO (s) + H_2O (l) + 2e^- \longrightarrow Hg (l) + 2OH^- (aq)$

$Zn(Hg) + HgO (s) \longrightarrow ZnO (s) + Hg (l)$

Batteries

Lead storage battery



Anode: $Pb\ (s) + SO_4^{2-}\ (aq) \longrightarrow PbSO_4\ (s) + 2e^-$

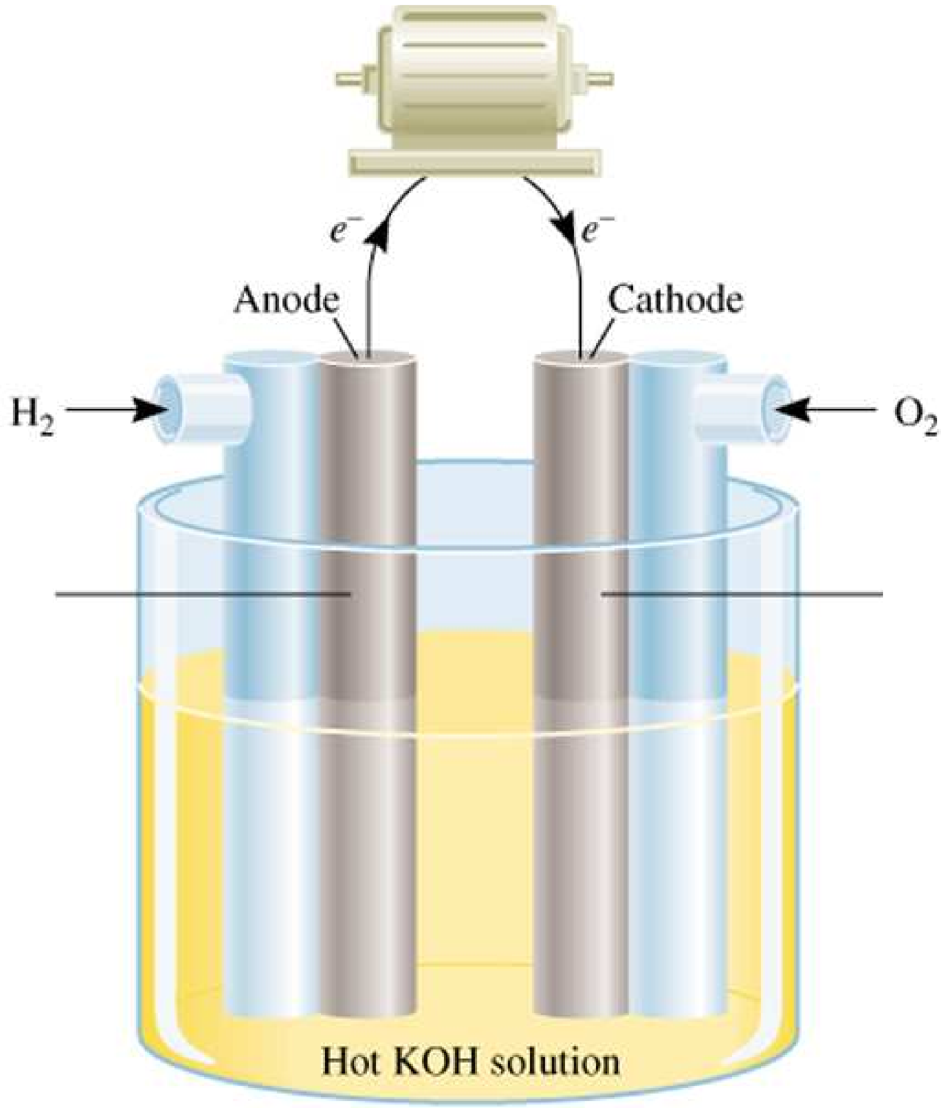
Cathode: $PbO_2\ (s) + 4H^+\ (aq) + SO_4^{2-}\ (aq) + 2e^- \longrightarrow PbSO_4\ (s) + 2H_2O\ (l)$

$Pb\ (s) + PbO_2\ (s) + 4H^+\ (aq) + 2SO_4^{2-}\ (aq) \longrightarrow 2PbSO_4\ (s) + 2H_2O\ (l)$

Fuel Cell vs. Battery

- Battery; Energy storage device
  - Reactant chemicals already in device
  - Once Chemicals used up; discard (unless rechargeable)

- Fuel Cell; Energy conversion device
  - Won't work unless reactants supplied
  - Reactants continuously supplied; products continuously removed



Fuel Cell

A ***fuel cell*** is an electrochemical cell that requires a continuous supply of reactants to keep functioning

Anode: $2H_2\,(g) + 4OH^-\,(aq) \longrightarrow 4H_2O\,(l) + 4e^-$

Cathode: $O_2\,(g) + 2H_2O\,(l) + 4e^- \longrightarrow 4OH^-\,(aq)$

$2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(l)$

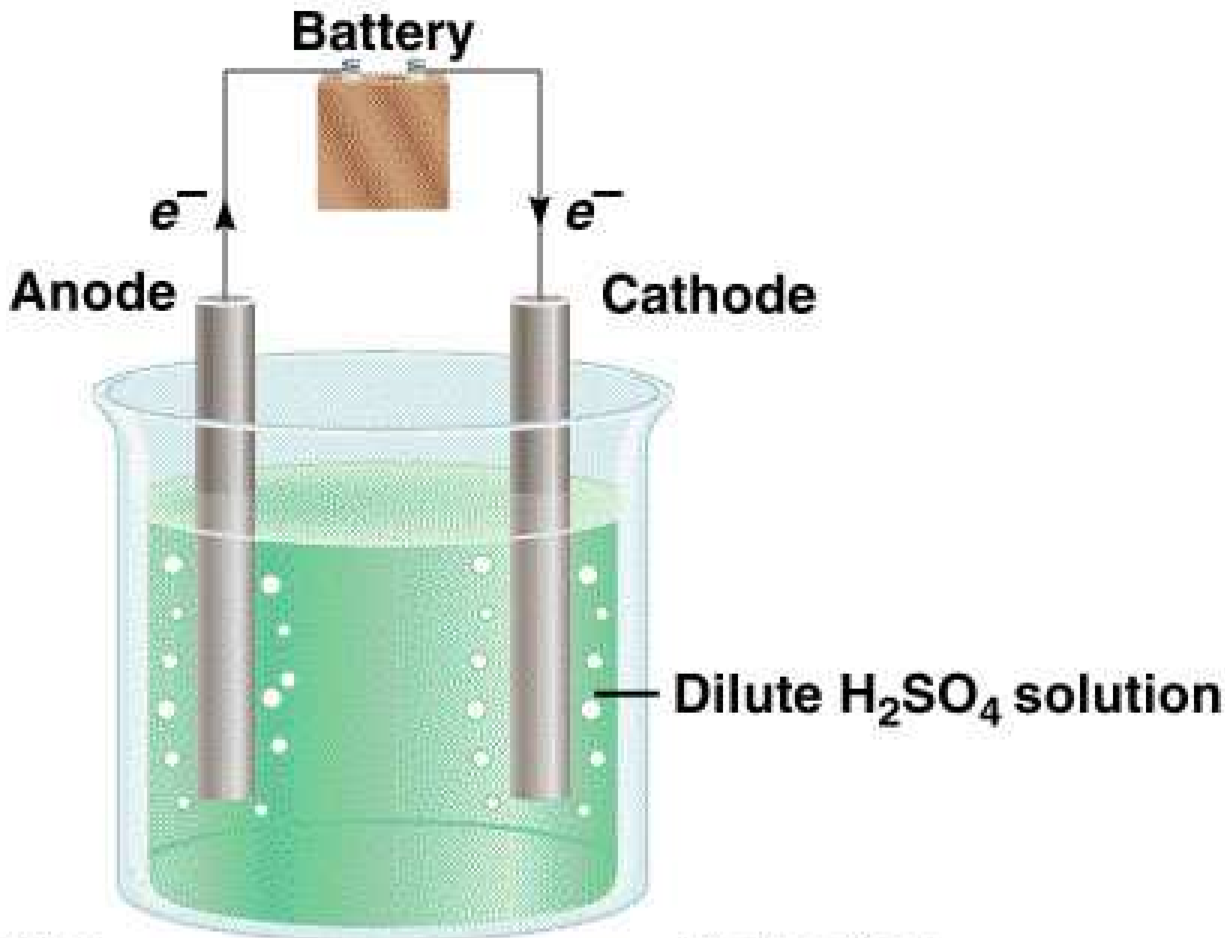
Types of Electrochemical Cells

- Voltaic/Galvanic Cell; Energy released from spontaneous redox reaction can be transformed into electrical energy.

- Electrolytic Cell; Electrical energy is used to drive a nonspontaneous redox reaction.

Small-Scale Electrolysis

Electrode Reactions during the Electrolysis of Water



Oxidation

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$$

Reduction

$$4H^+(aq) + 4e^- \longrightarrow 2H_2(g)$$

Electrolytic Purification of Copper